

THE APPLICATION OF CITRIC ACID SOLUTIONS FOR SELECTIVE REMOVAL OF ZINC FROM STEELMAKING DUST

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Abstract

Steelmaking dust is one of the wastes which are produced by ironworks. This kind of waste is a byproduct produced mainly in electric arc furnace. Zinc content in dust is different and depends on the charge processed in the furnace. The basic technology used for recycling steelmaking dust is Waelz process, however, it requires a large amount of reducer and generates a lot of waste which needs to be stored. First stage in this study was to analyze if steelmaking dust was safe to be exposed to atmospheric conditions. To verify this, the dust was subjected to two kinds of standard leaching tests, TCLP and EN-12457-2. The amount of extracted elements was considerable and that was why steelmaking dust should be treated as dangerous waste. Leaching in citric acid solutions was divided in four series. The first one was set to determine the time and temperature for most selective zinc leaching. Next series optimized three leaching parameters which were: citric acid concentration, liquid to solid phase ratio (l/s), and the stirring speed. Performed experiments showed the optimal conditions for selective leaching: temperature of 50 °C, leaching time of 60 minutes, citric acid concentration of 0.5 mol/dm³, l/s ratio of 10, and stirring speed of 250 rpm.

Keywords: Steelmaking dust; Citric acid; Zinc recovery; Leaching

1. Introduction

The world steel production increases every year, which also causes an increase in waste production. The main wastes from the steel industry are: slags, sludges and dusts. Despite their partial use by recycling or other recycling, not all waste is recycled. The basic material used for steel smelting are iron ores, containing hematite Fe₂O₃ and magnetite Fe₃O₄. Steel scrap is also used, which may contain elements such as zinc or lead. These metals have a relatively low boiling point, which is why they evaporate during the process and most are transferred to dusts or sludges. The world annual production of dust and sludge reaches about 61 million tons [1, 2].

Steel scrap recycling is an important part of the steel industry. The scrap metal can be fed into the electric arc furnace, but for quality reasons auxiliaries are needed. Additions to the charge allow you to maintain the high quality of the product and minimize contamination with other metals. Due to environmental protection, the amount of steel recycled in this type of furnace increases. Around 31% of the steel in the world is produced in electric arc furnaces [3]. However, this process creates significant amounts of dust containing iron, zinc, lead,

cadmium, and other elements. Some of the dust from this process is recycled, but it is a limited amount, because too much dust could damage the original processes by reducing the quality of the steel. Steelmaking dust from electric furnaces is rich in zinc from galvanized steel scrap.

There are many processes of dust processing, both pyrometallurgical and hydrometallurgical. To conduct these processes, a large amount of energy and process additives are needed, which leads to specific costs of processing and utilization of these materials. That is why steelmaking dust is becoming a growing problem in the context of waste materials on a global scale. Steel works generally try to use collected dust and sludge. Depending on the chemical composition of the dust, different procedures are implemented. If the zinc content in the material is low enough, it will be introduced as a charge into the blast furnace. Too much zinc entering the blast furnace can adversely affect the gas draft behind it. This metal can be recovered in a cost-effective way from waste with a high zinc content.

The composition of dust depends on the parameters of the steel that is produced, alloy additions, and the amount of scrap introduced into the process. There is a lot of iron in the dust, often in the

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form of Fe_3O_4 , about 50÷80% of zinc is bound in the form of zinc oxide, and the remainder of iron and zinc occurs as ZnFe_2O_4 . The formation of zinc ferrite is based on the contact of zinc particles with iron at high temperature under oxidative conditions. When galvanized steel is used for the process, most of the zinc goes to process gases. The reason is the higher vapor pressure of zinc than iron at process temperature. Zinc concentration in dusts can reach up to 40%, however, it is usually between 11-33% [4-9]. Iron is present in the material from 18% up to 47%, as oxides or bound in ferrite. Lead content is significantly lower and does not exceed 4.5%. Other elements in the samples appear in trace amounts and their content is shown in Table 1. About 23.5 million tonnes of sludge and dust from electric arc furnaces are produced annually, which is a serious problem in the context of environmental protection.

The most commonly used process for pyrometallurgical recycling of zinc waste is Waelz process. About 75% of steel dust processed by pyrometallurgical methods is used for this process [10]. This method is intended to evaporate most heavy metals (zinc, lead, and cadmium) and separate them from inert elements such as iron, silica, calcium, sodium, potassium, and magnesium. The movement of the material in the furnace is caused by the inclination of the furnace relative to the ground and the rotational movement during operation of the furnace. Prepared material is placed in furnace, where it is heated and dried by air passed in countercurrent [11]. Preheated charge moves to a zone where the temperature is 1100-1200 °C, in which metal oxides are reduced, and zinc and lead are evaporated. The

blown air is controlled so that metals mixture in gas phase is oxidized and removed with the process gases. The process gases are quenched and then go through a dust removal process, where zinc and lead oxides are separated from the rest of the process gases. This creates Waelz zinc oxide, otherwise known as raw zinc oxide, which is the final product of the process. Iron and other inert substances produced in the Waelz process in oxidized form are waste and are collected at the furnace outlet. The input must meet certain criteria, whose main indicator is a content of at least 18% Zn in steelmaking dust. In order to obtain this level of Zn, enrichment methods are used [12]. The final product is raw zinc oxide with a content of 55-58% Zn, which is purified to remove chlorides and fluorides, and then transferred to the electrolytic process for the production of zinc, or other hydrometallurgical or pyrometallurgical processes. The Waelz method is widely used, despite some restrictions such as a large amount of fuel and the need to use a reducer to carry out the process [13].

The best-known methods of hydrometallurgical processing of zinc-bearing waste materials are Zincex and Ezinex methods. Classic Zincex process and Ezinex process involves leaching metal oxides (ZnO , PbO , etc.) from dust in an acidic or alkaline solvents [14, 15]. Leaching solutions, such as sulfuric acid, allow good zinc recovery, but can also cause secondary waste and dissolve iron (e.g. up to 45%) even when using dilute sulfuric acid. Compared to acidic solvents, alkaline solutions (e.g. sodium hydroxide) are more selective. This approach can lead to better technical and economic results, with less waste generated. The disadvantage of alkaline

Table 1. Composition of steelmaking dust originating from various electric arc furnaces

Component	Colakoglu	ACERINOX	Outokumpu Tornio Works	Co-Steel Lasco	Ternium Brazil	Chaparral Steel of Midlothian
	(Turkey)	(Spain)	(Finland)	(Canada)	(Brazil)	(USA)
	[4]	[5]	[6]	[7]	[8]	[9]
(wt. %)						
Zn	33	29	24.8	31.2	12.2	20.5
Fe	26	25	32	18.3	37.08	21
Pb	3.05	4	1.84	1.02	1.72	4
SiO_2	3.15	3	-	3.41	-	0.4
Cu	0.24	0.3	0.02	-	0.17	0.38
Cd	0.05	0.07	0.03	-	0.01	0.18
Cr	0.24	-	-	0.19	0.22	0.19
Al	0.6	-	-	0.68	0.41	0.6
Mn	1.83	3	3.31	2.2	-	2.25
Ca	2.9	-	4.08	15.6	-	12.5
Na	1.03	-	-	3.8	-	1
K	0.85	-	-	0.67	-	0.68



leaching is unwanted lead leaching.

The purpose of this work is to study the behavior of zinc and iron in the leaching of steelmaking dust from electric arc furnaces with citric acid solutions. A series of experiments were planned to provide information on the behavior of the above-mentioned metals under leaching conditions with the following parameters changing:

- temperature,
- time,
- citric acid concentration,
- liquid to solid ratio, and
- mixing speed.

Optimization of leaching parameters leads to such a set at which the maximum ratio of zinc to iron leaching is efficiently obtained. The solution containing a small amount of iron produced after leaching will allow easier recovery of zinc from the solution. It could be made in several ways. Zinc could be precipitated as insoluble salt, the solution could be electrolyzed, liquid ion exchangers could be used, or else pressure reduction with hydrogen gas could be carried out [16, 17].

2. Properties of used materials

2.1. Chemical and phase composition

Steelmaking dust from one of the Polish plants utilizing steel scrap in electric arc furnaces was used for the tests. The chemical composition of dusts was determined by two methods: first, with the approximate XRF method without reference materials, followed by ED XRF with zinc and iron standards. Using these methods, both the chemical and phase composition of the tested sample was determined. Table 2 presents the results of the chemical composition analysis in a wide elemental range (without reference materials). Accurate determination of zinc and iron in the sample required

Table 2. Elemental composition of the initial sample of steelmaking dust

element	content (wt. %)
Fe	33.64
Zn	25.7
Ca	3.13
Mn	2.11
Mg	1.67
Pb	1.6
K	1.31
Si	1.46
Cl	0.95
S	0.58
Al	0.29
Cr	0.22
Cu	0.22
P	0.07

is obtained by a standard XRF analysis. To this end, zinc and iron (III) oxide powders were mixed in various proportions. The following reagents were used: Zinc Oxide (ZnO) Sigma-Aldrich, >99.0% and Iron (III) oxide (Fe₂O₃) Sigma Aldrich, >96.0%. The content of iron and zinc in the mixtures was strictly determined. The standards were mixed so that the content in the individual was equal to 5%, 10%, 15%, 20%, 25%, and 45%. The R² coefficient for the zinc calibration curve was 0.9964 and for iron was 0.9982. The course of calibration curves is shown in Figure 1. The standard analysis shows that the original sample contained 22.22% Zn and 32.09% Fe.

In order to determine the main phases occurring in the tested steelmaking dust, XRD analysis was performed. The main compounds identified in the tested dust were franklinite and zinc oxide. In addition to them, potassium chloride was also detected. The

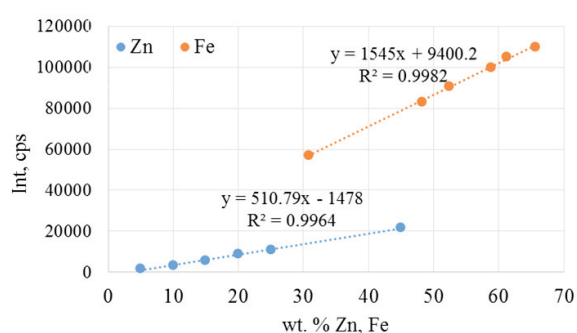


Figure 1. Calibration curves of zinc and iron

results of the XRD study are shown in Figure 2. SEM analysis of steelmaking dusts was also carried out. The obtained results are shown in Figure 3. One can notice quite a large variation in the zinc content in the analyzed grain with a relatively stable iron content.

2.2. Toxicity characteristic of steelmaking dust

Waste materials from steel production processes, i.e. steelmaking dust, are usually stored in heaps. This

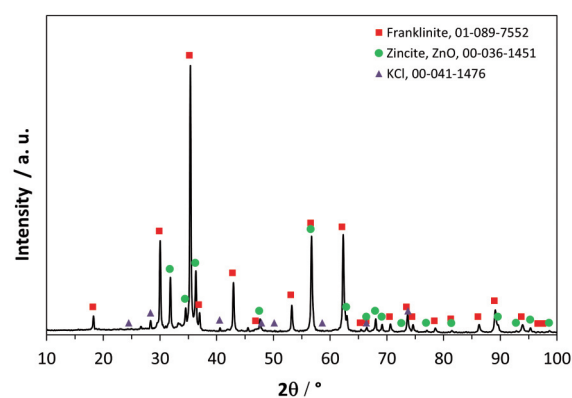


Figure 2. XRD of steelmaking dust



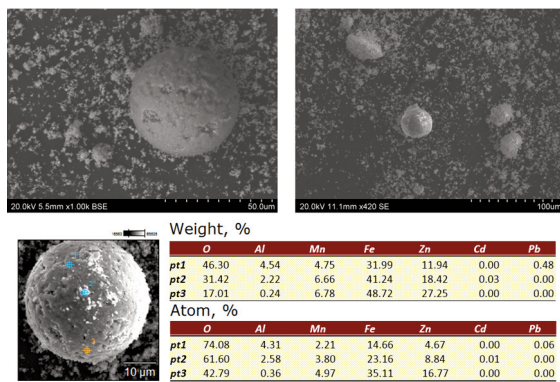


Figure 3. SEM analysis of the initial steelmaking dust sample

exposes the material to atmospheric agents, which may cause leaching of chemicals that are hazardous to the environment. Therefore, washing tests were conducted as part of this study to determine whether the material was hazardous to the environment. Leaching tests were carried out according to EN-12457-2 [18] and TCLP (Toxicity Characteristic

Table 3. Elemental concentrations in the solution and in the dry sample after test according to EN-12457-2

element	concentration - effluent (mg/dm ³)	concentration - dry sample (mg/kg)	max concentration according to the standard (mg/kg)
As	0.025	0.25	0.05
Sb	0.006	0.06	0.08
Ba	0.061	0.61	6.2
B	2.036	20.36	1.96
Pb	0	0	1.2
Cu	0	0	0.19
Mo	0.735	7.35	1.12
Zn	0.01	0.1	5.31

Table 4. Elemental concentrations in the solution after the test according to TCLP

element	concentration (mg/dm ³)	max concentration (mg/dm ³)
Zn	876	250
As	0	5
Ba	0.5	100
Cd	2.34	1
Cr	0.01	5
Pb	38.76	5
Hg	0	0.2
Se	0	1
Ag	0	5

Leaching Procedure) [19]. The effluents were examined by the ICP OES method and the concentration of eluted elements was obtained in mg/l. The verification of the results obtained for the TCLP standard consisted only of a direct comparison of the numerical values, while for the EN-12457-2 standard the concentrations obtained in the solution were converted into the mass of the element carried into the solution per 1 kg of dry sample. The obtained results are presented in Table 3 (EN-12457-2) and 4 (TCLP).

Presented results indicate that, in relation to the EN-12457-2 regulation, the levels of arsenic, boron, and molybdenum acceptable concentration were exceeded. In the case of the leaching test according to the TCLP standard, significant exceeding of the levels for Zn, Cd, and Pb was obtained. This dust, in accordance with the conducted research, should be considered as hazardous waste for the environment and processed in the direction of obtaining environmentally neutral material.

2.3. Sieve analysis of used material

The sieve analysis was carried out in order to determine the share of individual grain fractions in the tested steelmaking dusts, as well as to examine the concentration of zinc and iron in individual grain classes. The presence of a fraction in which the content of one of the metals would differ significantly from the average content in the averaged sample would give the opportunity to extract it from the whole material and separate processing. Figure 4 presents the share of grain fractions after sieve analysis. The tested material was dominated by the 0.4-0.63 mm fraction. Its share was 38.67% and it was more than twice as large as the second in terms of size 0.32-0.4 mm. Individual grain classes were tested for zinc and iron content by the ED XRF method.

Figure 5 shows the zinc content in individual grain classes, which were similar and remained at over 20%. Only for class <0.056 mm the content dropped to 15%. The maximum zinc content (23.28%) was recorded in the 0.16-0.2 mm fraction. Figure 6 shows

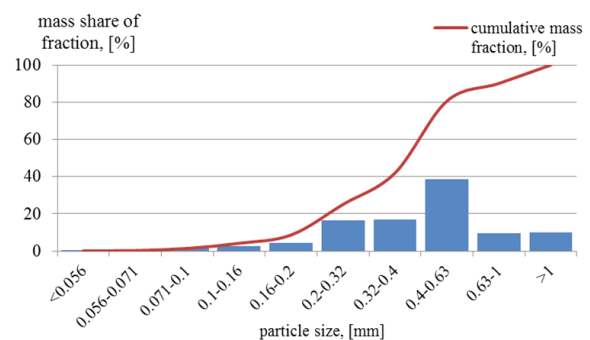


Figure 4. Grain analysis of steelmaking dusts

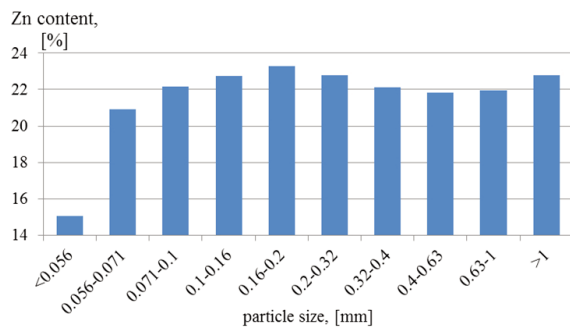


Figure 5. Zinc content in individual grain classes of steelmaking dust

the varied iron content in the steelmaking dust sample. It is not possible to indicate any trend of the obtained results, but the iron content did not exceed 36% or fell below 30%. The maximum iron content of 35.75% was found in the 0.16-0.2 mm fraction and the lowest 30.76% in the 0.4-0.63 mm fraction. Summarizing, fraction 0.16-0.2 mm had the highest content of zinc and iron among the rest of the grain classes.

3. Leaching of steelmaking dusts with citric acid solutions

In this paper, it was decided to conduct zinc and iron leaching tests from steelmaking dust using citric

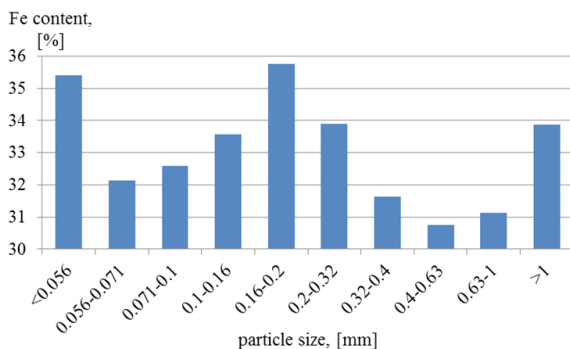
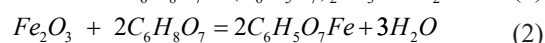
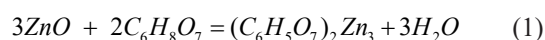


Figure 6. Iron content in individual grain classes of steelmaking dust

acid solutions. Citric acid allows the transfer of lead to the solution during processing lead-acid batteries [20], copper or lead during recycling flash smelting slag from copper industry [21], or nickel and copper during processing of PCBs [22]. When processing steelmaking dust, iron and zinc may pass into solution in accordance with the following reactions:



Leaching process was carried out under certain

conditions of time, temperature, citric acid concentration, l/s ratio, and mixing speed. After leaching, the mixture was filtered, washed, dried, weighed, and then chemical analysis of Zn and Fe content by ED XRF was carried out.

Leaching and optimization of parameters was carried out in the direction of obtaining the maximum zinc leaching efficiency with the minimum values of this parameter in relation to iron. Thus, the process was to be selective with respect to zinc.

The test stand (Figure 7) consisted of a water bath in which 800 ml beaker for leaching solution was placed. An external thermometer was used to measure the temperature of the solution in the beaker, and verify the temperature against the temperature set in the bath. A mechanical stirrer was placed in the beaker to ensure leached material movement in the entire volume of the solution. After leaching, the entire mixture was filtered on a Büchner funnel, and the resulting material was washed with distilled water. Sludge obtained after leaching was analyzed for Zn and Fe content by XRF method and some of the samples by XRD method. First, the influence of parameters such as temperature and leaching time was examined in order to select optimal leaching conditions from the point of view of selective leaching of zinc.

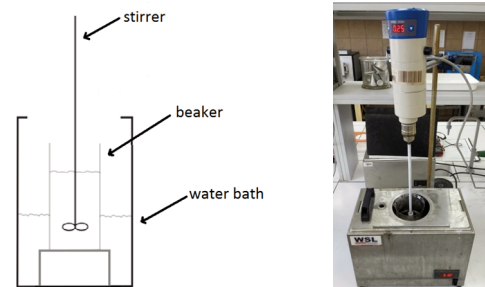


Figure 7. Test stand for steelmaking dust leaching

After determining the optimal leaching time and temperature, further parameters such as acid concentration, liquid to solid phase ratio, and mixing speed were optimized until a complete set of parameters was obtained. The results after each of the conducted stages were calculated in order to determine the zinc leaching efficiency in accordance with the relationship:

$$\eta_{Zn} = \left(\frac{m_{Zn}^0 - m_{Zn}}{m_{Zn}^0} \right) \cdot 100\% \quad (3)$$

where:

m_{Zn}^0 - mass of zinc in the sample before the process

m_{Zn} - mass of zinc in the sample after the process

Iron leaching efficiency was determined according



to the relationship:

$$\eta_{Fe} = \left(\frac{m_{Fe}^0 - m_{Fe}}{m_{Fe}^0} \right) \cdot 100\% \quad (4)$$

where:

m_{Fe}^0 - mass of iron in the sample before the process

m_{Fe} - mass of iron in the sample after the process

Leaching selectivity ϵ was determined by the ratio of zinc leaching efficiency to iron leaching efficiency:

$$\epsilon = \frac{\eta_{Zn}}{\eta_{Fe}} \quad (5)$$

where:

η_{Zn} - zinc leaching efficiency

η_{Fe} - iron leaching efficiency

3.1. Leaching time and temperature optimization

The first stage of leaching steelmaking dust with citric acid solutions was carried out under the conditions of fixed parameters of citric acid concentration (1 mol/dm³), l/s ratio equal to 10 ml/g, and the rotational speed of the mixer (250 rpm). A weight of 40 g steelmaking dusts was leached in 400 ml citric acid solution. The process was carried out at 25 °C, 50 °C, and 70 °C for 30, 60, and 120 minutes. The results obtained are shown in Table 5 and Figure 8. The results obtained indicated that changes in conditions affected the leaching efficiency of both zinc and iron. It can be seen that in most cases, the higher temperature and the longer leaching time, the more efficient the process. The ratio of zinc to iron leaching efficiency ϵ was the highest in the test carried out at 50 °C and for a time of 60 minutes. The factor

ϵ obtained a value approaching 13 at that time.

The investigation of the first series showed that the zinc and iron leaching efficiency decreased after reaching a certain maximum. A deviation from this

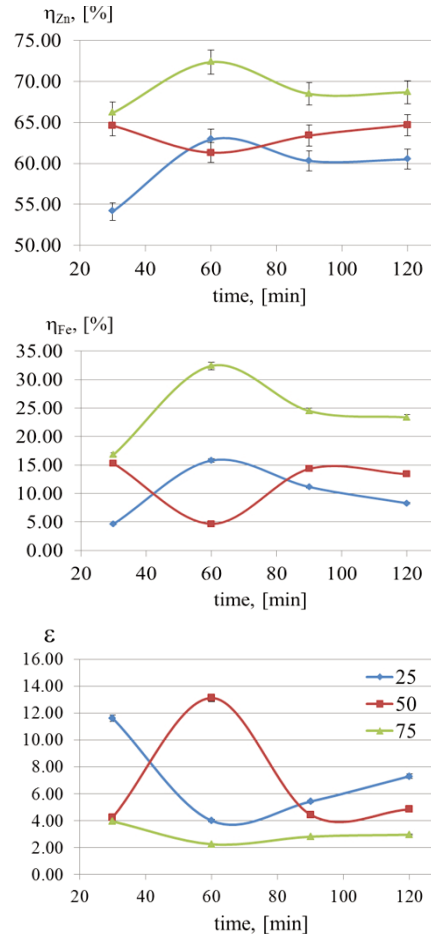


Figure 8. Zinc and iron leaching efficiency and zinc to iron leaching efficiency factor ϵ at different temperatures (25 °C, 50 °C and 75 °C) vs. leaching time

Table 5. Results obtained in leaching tests during optimization of process time and temperature

temp. (°C)	time (min)	sample weight (g)	pH ₀	pH ₁	final mass (g)	Zn	Fe	η_{Zn}	η_{Fe}	ϵ				
						(wt.%)	(wt.%)	(%)	(%)					
25	30	40	2.16	3.08	27.75	14.7	44.1	54.1	4.7	11.61				
	60			3.01	22.9	14.4	47.2	62.9	15.8	3.98				
	90			3.1	24.01	14.7	47.5	60.3	11.2	5.41				
	120			3.12	25.26	13.9	46.6	60.5	8.3	7.29				
50	30			40	2.77	3.41	23.29	13.5	46.7	64.6	15.3	4.23		
	60					3.4	25.28	13.6	48.4	61.3	4.7	13.11		
	90					3.71	23.4	13.9	47	63.4	14.3	4.43		
	120					3.3	23.6	13.3	47.1	64.7	13.4	4.83		
75	30					40	3.62	4.15	22.29	13.5	47.9	66.1	16.8	3.93
	60							4.21	18.19	13.5	47.7	72.4	32.4	2.23
	90							4.47	20.15	13.9	48.1	68.5	24.5	2.8
	120							4.37	20.93	13.3	47	68.7	23.4	2.94



regularity was observed in the case of iron leaching at a temperature of 50 °C and this affected the high value of the ε coefficient. The decrease in zinc and iron leaching efficiency at 120 minutes leaching compared to the yields obtained after 60 minutes was decided to interpret based on XRD analysis of materials obtained after testing.

Analysis of XRD diagrams (Fig. 9) indicated that no ZnO phase was observed in the sample obtained after 60 minutes of leaching, and ZnO was observed in the obtained material after a leaching time of 120 minutes. Presumably, filtration at a temperature lower

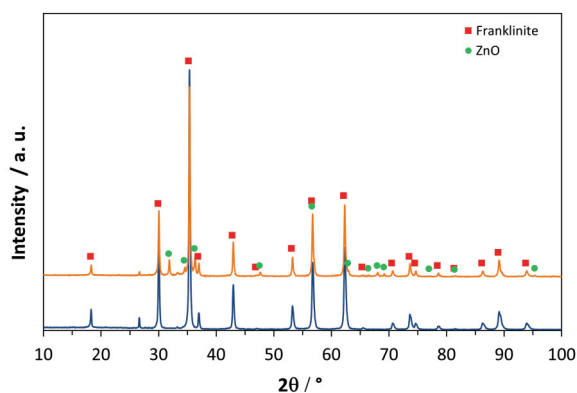


Figure 9. XRD phase analysis of samples after leaching during 60 (orange line) and 120 minutes (blue line) (75 °C)

than 75 °C led to a shift in the equilibrium of the reactions (1) and (2) towards the substrates and precipitation of solid ZnO from solution. For further research, it was assumed that from the point of view of leaching selectivity, the leaching of steelmaking dust should be continued at temperature and time parameters of 50 °C and 60 minutes, respectively.

3.2. Effect of citric acid concentration on Zn and Fe leaching from steelmaking dust

After determining the optimal time and temperature of steelmaking dust leaching, subsequent parameters were optimized. Another changed parameter was the concentration of leaching solution (from 0.5 mol/dm³ through 1 mol/dm³ to 2 moles/dm³). Each leaching test in this series was carried out for 60 minutes at 50 °C, liquid to solid phase ratio (l/s) was 10 and the mixing speed was 250 rpm. The results of the measurements are presented in Table 6 and Figure 10.

Table 6. Summary of results obtained in leaching tests during optimizing of citric acid concentration

citric acid concentration (mol/dm ³)	sample weight (g)	pH ₀	pH ₁	final mass (g)	Zn (wt.%)	Fe (wt.%)	η_{Zn} (%)	η_{Fe} (%)	ε
0.5		3.56	4.49	24.55	13.6	48.4	61	3.8	16.21
1	40	2.77	3.4	25.28	13.6	48.4	61.3	4.7	13.11
2		2.2	2.6	22.63	13.4	45	65.9	17.4	3.19

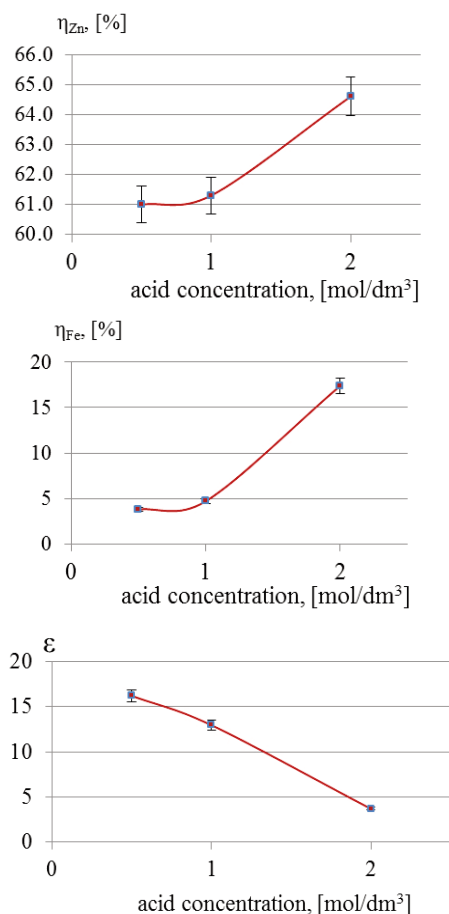


Figure 10. Zinc and iron leaching efficiency and zinc to iron leaching efficiency factor ε vs. citric acid concentration

During tests where the citric acid concentration was a variable parameter, the amount of leached zinc and iron increased as the acid concentration increased. The higher the reagent concentration, the lower the ε factor. Zinc was most selectively leached out when a solution with citric acid concentration of 0.5 mol/dm³ was used. The coefficient ε then obtained a value above 16.

3.3. Optimization of liquid to solid phase ratio (l/s)

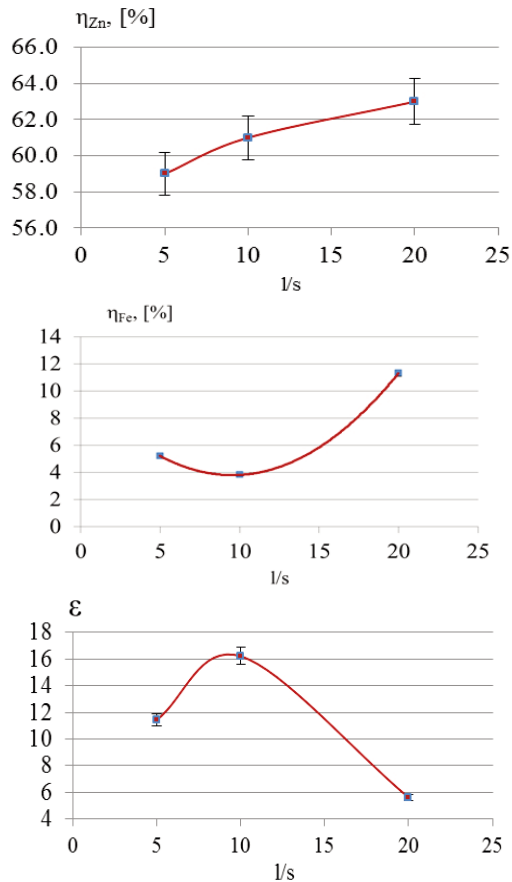
After optimization of citric acid concentration, another parameter to be changed was liquid to solid phase ratio (l/s) (from 5 to 10 to 20). Each leaching test in this series was carried out for 60 min at 50 °C, in a solution with citric acid concentration of 0.5

Table 7. Summary of results obtained in leaching tests during l/s ratio optimizing

l/s	sample weight (g)	pH ₀	pH ₁	final mass (g)	Zn (wt.%)	Fe (wt.%)	η _{Zn} (wt.%)	η _{Fe} (wt.%)	ε
5	40	3.56	4	26.48	13.8	46	59	5.2	11.44
10			4.49	24.55	13.6	48.4	61	3.8	16.21
20			3.95	12.35	13.3	46.1	63	11.3	5.6

mol/dm³, at a mixing speed of 250 rpm. The measurement results are presented in Table 7 and Figure 11.

The tests showed that the highest value of the ε coefficient was obtained with l/s ratio of 10.

**Figure 11.** Zinc and iron leaching efficiency and zinc to iron leaching efficiency factor ε vs. l/s ratio

3.4. Impact of mixing speed on the leaching process

The last parameter that was optimized in this study was the rotational speed of the mixer. Each leaching in this series was carried out for 60 minutes at 50 °C, citric acid concentration was 0.5 mol/dm³, and liquid to solid phase ratio was 10. The rotational speed was changed from 150 to 250 to 350 rpm. The results of the measurements are given in Table 8 and Figure 12.

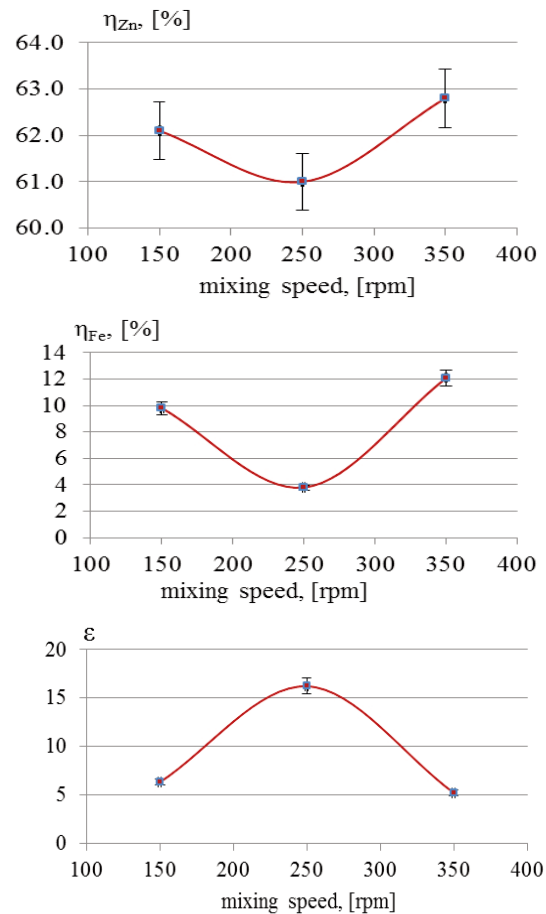
The obtained results indicated that the highest

Table 8. Summary of results obtained in leaching tests during rotational speed optimizing

mixing speed (rpm)	sample weight (g)	pH ₀	pH ₁	final mass (g)	Zn (wt.%)	Fe (wt.%)	η _{Zn} (%)	η _{Fe} (%)	ε
150	40	3.56	4.31	25.39	13.30	45.60	62.10	9.80	6.33
250			4.49	24.55	13.60	48.40	61.00	3.80	16.21
350			4.27	25.14	13.20	44.90	62.80	12.10	5.2

selectivity of zinc leaching was obtained at the rotational speed of the mixer of 250 rpm.

The sample with the best selectivity of zinc

**Figure 12.** Zinc and iron leaching efficiency and zinc to iron leaching efficiency factor ε vs. mixing speed

leaching was subjected to XRD test and SEM analysis to determine the compounds present in this material (Fig. 13) and to determine the elemental composition at four selected points (Fig. 14). It can be seen that only franklinite was generally identified in this material. Thus, it can be assumed that the ZnO compound phase was completely leached, and the iron entering the solution originated from slightly leached franklinite.

The solution after leaching under optimized conditions ($\varepsilon = 16.21$) was subjected to ICP OES analysis to determine the content of elements. Their concentrations were: 17.24 g/l Zn, 3.68 g/l Ca, 2.97 g/l Fe, 1.93 g/l S, 1.78 g/l K, 1.47 g/l Si, 1.44 g/l Na, 1.01 g/l Pb, 0.5 g/l Mg, and 0.36 g/l Mn.

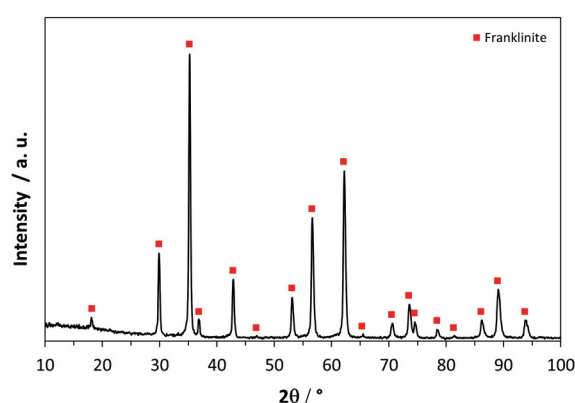


Figure 13. XRD analysis of the leached sample with the highest parameter ε

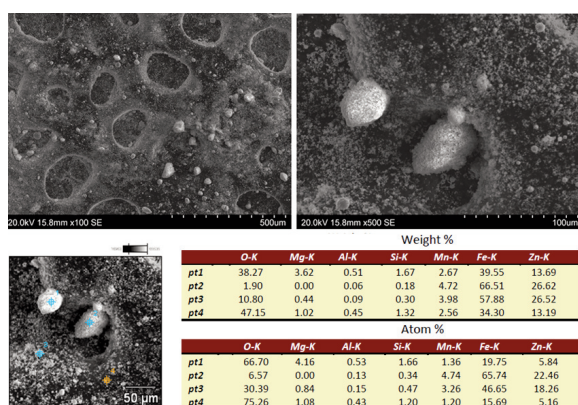


Figure 14. SEM analysis of steelmaking dust sample after leaching with the highest parameter ε

4. Results and Discussion

Sieving tests of steelmaking dust analyzed in this work were quite homogeneous in terms of zinc and iron content. Therefore, it was not possible to select a fraction in which there was an increased content of zinc or iron and separate processing of such a fraction in the iron production process or recycling in the

direction of zinc recovery.

Samples of steelmaking dust were subjected to leaching tests in accordance with EN-12457-2 and TCLP. It was found that the permeate values of some elements were exceeded in the leachate. Testing in accordance with EN-12457-2 showed that the permissible values of arsenic, boron, and molybdenum were present in the solution in excess of. In the case of leaching tests in accordance with the TCLP standard, the permissible amounts of eluted components such as cadmium, lead, and zinc were exceeded. Accordingly, steelmaking dust with this composition should be classified as hazardous material.

The main purpose of this work was to determine the possibility of using citric acid solutions for the selective extraction of zinc from steelmaking dust. Therefore, four series of tests were carried out during which leaching parameters, such as time, temperature, citric acid concentration, l/s ratio, and rotational speed of the mixer were optimized. These tests indicated the possibility of selective leaching of zinc from steelmaking dust. This was mainly possible due to the specific course of the iron leaching curve during the process carried out at 50 °C. Then, after 60 minutes, the minimum leaching efficiency was recorded. In the other variants of zinc and iron leaching, the efficiency of the process was a monotonically increasing function over time. The consequence of these two facts was the appearance of a high factor ε in the place where the minimum iron leaching efficiency occurred. Optimization of all leaching parameters led to their set where the coefficient ε obtained the highest value of 16.21. Optimized parameters were temperature equal to 50 °C, leaching time - 60 minutes, concentration of the citric acid solution of 0.5 mol/dm³, parameter l/s equal to 10, and mixing speed equal to 250 rpm. XRD examination of a sample of the material after leaching under optimized conditions showed that there was only one phase in it, which was franklinite. Therefore, all the zinc present in the ZnO form was transferred to the solution, and the iron identified in the solution originated from the franklinite, which was decomposed slightly by citric acid.

Performed research allowed to observe an increase in the zinc content in the sample at the longest leaching time compared to the shorter leached dust. In order to determine the nature of such a phenomenon, the sample with the highest zinc leaching efficiency (60 minutes) and the one after the decrease in efficiency (120 minutes) were examined by XRD method. The main difference between the results of performed analyzes was the identification of the zinc oxide phase in the sample obtained after leaching for 120 minutes. It should be assumed that the high leaching temperature led to a significant shift in the

reaction balance between ZnO and citric acid towards the formation of zinc citrate. However, the leach mixture filtration process typically occurred at a lower temperature than the leaching temperature, and the process was not instantaneous. Solution therefore lowered its temperature, the equilibrium of the leaching reaction shifted towards the substrates and, as a consequence, precipitation of solid ZnO from solution occurred and the zinc leaching efficiency decreased. A remedy for this kind of phenomenon would be to carry out the filtration process in conditions of pre-elevated temperature of the filtration equipment so as to eliminate the possibility of precipitation of solid reagents from the solution. The weight of the leach residue was reduced by about 40% compared to the initial weight of steelmaking dust. This material could be processed in the Waelz process or another reduction remelting for the selective recovery of zinc and iron [23].

5. Conclusions

The research carried out in this work allowed to formulate the following conclusions:

- steelmaking dusts was the homogeneous material in terms of zinc and iron content, regardless of the grain class,
- leaching tests showed that steelmaking dust was a hazardous material from the point of view of its impact on the natural environment and was not suitable for long-term storage under atmospheric conditions,
- selective leaching of zinc from steelmaking dust with citric acid solutions was possible,
- changing leaching conditions affected the leaching efficiency of iron and zinc, and hence the leaching selectivity,
- citric acid was a relatively weak acid and readily dissolved zinc found in steelmaking dust in the form of ZnO; franklinite leaching was more difficult, hence the possibility of selective leaching of zinc with minimal iron leaching efficiency,
- in conditions of long-term leaching of steelmaking dust and long-term mixture filtration, especially at a falling temperature at this stage of the process, precipitation of zinc compounds and a decrease of zinc leaching efficiency occurred.

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PRIMENA RASTVORA LIMUNSKKE KISELINE ZA SELEKTIVNO UKLANJANJE CINKA IZ PRAŠINE NASTALE U PROCESU PROIZVODNJE ČELIKA

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Apstrakt

Prašina predstavlja jednu vrstu otpada koja nastaje prilikom proizvodnje čelika. Ova vrsta otpada predstavlja nusproizvod koji uglavnom nastaje u elektrolučnoj peći. Sadržaj cinka u prašini se razlikuje i zavisi od šarže koja se koristi u peći. Osnovna tehnologija koja se koristi za reciklažu prašine iz procesa dobijanja čelika je Waelz proces, međutim, on zahteva veliku količinu reducenata i stvara mnogo otpada koji treba skladištiti. Prva faza ovog istraživanja je podrazumevala analizu sigurnosti izlaganja prašine atmosferskim uslovima. Kako bi se ovo utvrdilo, prašina je podvrgnuta standardnim testovima izluživanja TCLP i EN-12457-2. Količina ekstrahovanih elemenata je bila značajna i zbog toga bi prašinu trebalo tretirati kao opasan otpad. Luženje u rastvoru limunske kiseline je bilo podeljeno u četiri faze. Tokom prve faze je utvrđeno vreme i temperatura za najselektivnije luženje cinka. Tokom narednih faza optimizovana su tri parametra luženja, koncentracija limunske kiseline, odnos tečno/čvrsto i brzina mešanja. Izvedeni eksperimenti su pokazali da su optimalni uslovi za selektivno luženje sledeći: temperatura 50°C, vreme luženja 60 minuta, koncentracija limunske kiseline 0,5 mol/dm³, odnos tečno/čvrsto 10 i brzina mešanja 250 rpm.

Ključne reči: Prašina iz procesa proizvodnje čelika; Limunska kiselina; Dobijanje cinka; Luženje

